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| <b>(54) Title:</b> METHOD FOR TREATING FERROUS SULPHATE<br><br><b>(57) Abstract</b><br><p>The invention concerns a method for treating ferrous sulphate for the preparation of ferrous sulphate hydrate usable for chromium reduction in cement manufacture. According to the invention, sulphuric acid containing ferrous sulphate obtained as a side product from titanium dioxide production and which contains at the most appr. 30 % by weight of sulphuric acid, is neutralized with a CaO-containing material, preferably cement, in an amount sufficient to give a pH-value to the end product which is 1.5 to 5, whereby the reaction temperature is allowed to increase to at the most 120 °C.</p>  |           |  |

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# Method for treating ferrous sulphate

The object of the present invention is a method for treating ferrous sulphate for the preparation of ferrous sulphate hydrate which can be used in cement manufacture for the reduction of chromium.

As is known, cement is manufactured from limestone, silicate, iron and aluminium minerals together with optional fluorine and sulphur correction materials, which are ground and mixed homogenously and thereafter burned to form so called cement clinker. Cement also contains chromium compounds, which on contact with water, for example in concrete production, is converted to the  $\text{Cr}^{6+}$ -form.

This soluble chromate is undesirable as it can cause allergies in persons who come into contact with the cement-water mixture. It is known (e.g. EP 0054314), in order to reduce the  $\text{Cr}^{6+}$ -content, to add ferrous sulphate to the dry cement clinker to reduce  $\text{Cr}^{6+}$  to  $\text{Cr}^{3+}$ , which reduced form is practically insoluble in the cement-water mixture. The added amount ferrous sulphate is generally in the range of 0.5 to 1 % by weight of the cement clinker.

Ferrous sulphate has a tendency to absorb water wherefore it is difficult to handle as such, for example to pump or to blow. Ferrous sulphate is, however, commercially available e.g. in the form of its heptahydrate provided with an oxidation preventing coating, which coating imparts to the product also desirable flow characteristics. The use of such a coated preparation is, however, expensive taking into account the large amounts needed in cement manufacture. It has also been suggested (FI 842873) to use technical or commercial ferrous sulphate heptahydrate without said coating, whereby the ferrous sulphate heptahydrate first is subjected to drying by heating or absorption using physical or chemical methods. Mixing of gypsum or fly ash in the ferrous sulphate is mentioned as a particularly suitable chemical method, whereas calcium

oxide or cement alone are not said to give optimal results.

The problem underlying the present invention was to find  
5 a material for chromium reduction which, on the one hand,  
contains only such components that are "familiar" in cement  
manufacture and, on the other hand, are available at  
low cost and in large quantities, and the use of which in  
10 addition satisfies the environmental requirements one  
today places on the industry and its waste products. The  
problem according to the invention was solved by using,  
as chromium reduction agent, ferrous sulphate originating  
from the titanium pigment manufacture. The ferrous content  
15 in such a ferrous sulphate side product, which primarily  
in its monohydrate form, lies typically in the range of  
from 13 to 18 % by weight and it has a high sulphuric  
acid content, up to 30 % by weight, typically from about  
10 to 30 % by weight, and is therefore extremely  
20 corroding and useless as such. This product contains in  
addition a considerable amount of moisture, up to 10 % by  
weight, and smaller amounts of trace elements. It is a  
product which is extremely difficult to handle and a burden  
on the environment, and has to be neutralized in order  
25 to be deposited. Such methods according to which the  
neutralization takes place in an aqueous solution to an  
alkaline pH, have been described, for example, in DE OS  
4103311 and 3724677.

According to the invention, this moist and sulphuric acid  
30 rich ferrous sulphate obtained as a side product is neutralized  
and dried with a CaO-containing material, preferably cement,  
optionally together with limestone, to a pH-value of 1.5 to 5,  
thereby allowing the reaction temperature to rise to at the most  
120 °C. In the reaction,  
35 a large part of both the free water and the water bound in  
crystal water form leaves, and as major products ferrous  
sulphate hydrate, which is water soluble, primarily

in the form of monohydrate, and gypsum, calcium sulphate, which is one of the starting materials in cement production, are obtained.

- 5 It is essential that the temperature does not exceed the said 120 °C in order to ensure that not all hydrate water leaves the product and that the iron is not oxidized to trivalent form which is useless for the chromium reduction. The product obtained has excellent handling, especially flow characteristics, and it can be pumped and  
10 blown in silos, and it does not dust, which is of essential importance in industry in outdoor handling.

- Thus, according to the invention, a method has been provided according to which a waste product from the titanium dioxide pigment industry in a simple and economical manner can be converted to a product which is easy to handle and which without any problems can be further utilized in full in cement manufacture. The product contains  
15 only such components which are already included among the cement manufacture materials and thus does not contribute with any side products whatsoever which are detrimental to the cement manufacture.

- 25 As CaO-containing material, cement or a cement containing material, e.g. slag or fly ash cement, optionally together with limestone, are used. The CaO-containing material is added to the starting ferrous sulphate in substantially dry form. It is in principle possible to use  
30 any type of CaO-containing material, for example steel slag, blast furnace slag, precipitator dust etc. provided they exhibit sufficient hydraulic characteristics. Products having a lower reactivity, e.g. filter dust from the cement and lime industry, limestone, and even fly  
35 ash, are usable in an initial stage of the process, but in such case a post-treatment with more reactive material, e.g. cement, has to be carried out. It is also con-

ceivable to use hydrated and unhydrated lime, but the use of these extremely reactive materials require a strict temperature control.

- 5 The amount of CaO-containing material to be added depends naturally on the sulphuric acid content in the starting material, but an amount of from 5 to 20 % by weight, calculated from the starting ferrous sulphate, is in most cases sufficient to neutralize to the desired pH and to  
10 dry the product. The starting ferrous sulphate is used in the form it is obtained from the pigment production, that is in crystallized, filter dry pressed form, which generally means a moisture content of less than appr. 10 % by weight in the starting product. It is also possible to  
15 carry out a careful pre-drying of the starting material. The addition of CaO-containing material leads to an exothermic reaction, which aids in the removal of free moisture from the material. Care has to be taken, however, that the temperature does not rise too much, for the above reasons, which conveniently can take place by regulating the amount and rate of addition of neutralizing agent, but also by suitably choosing the degree of fineness of the material.
- 20
- 25 The flow characteristics of the obtained product can be further improved by treating the product with fly ash, either already together with the neutralizing material or after neutralization, using an amount up to 20 % by weight of the ferrous sulphate. Fly ash as such does not  
30 possess sufficient hydraulic properties to function alone as both a neutralization and drying medium, but can very well be used as a post-treatment agent, or filler.

- 35 According to an advantageous embodiment of the invention, the neutralizing agent, preferably cement, optionally together with limestone, is added in an amount which gives a pH of appr. 3 to 4. It is also preferable to keep

the temperature below appr. 105 °C, optimally at appr. 80 to 105 °C, whereby a soluble product suitable for passivation, is obtained. According to a preferred embodiment, the treatment can take place so that in a first stage  
5 limestone is added, which, as mentioned above, gives a slower reaction and a lesser temperature increase, for example to a pH of appr. 1.4, and thereafter the more active material, e.g. cement, is added to raise the pH to the desired pH end value. This procedure provides an excellent temperature control. If such a pre-treatment is  
10 carried out, the amount of cement or a material with comparative reactivity can be reduced, for example to 2 to 15 % by weight of the starting material. The pH value is measured by dissolving one part by weight of ferrous sulphate in 9 parts by weight of water.  
15

The composition of the product obtained after the treatment varies to some degree depending on the composition of the starting material and the amount and type of neutralizing agents used. From the point of view of use, naturally the ferrous content, i.e. the  $\text{Fe}^{2+}$ -content, is of importance, and this is generally within the range of 10 to 18 % by weight, which corresponds to a ferrous sulphate content in pure hydrate form of appr. 30 to 55 % by  
20 weight. In addition, the product typically contains appr. 15 to 30 % by weight of gypsum,  $\text{CaSO}_4$ , and moisture, typically 2 to 5 % by weight, and other products, e.g. cement and limestone. The product is well preserved during cement manufacture, i.e. there is no premature oxidation to  
25  $\text{Fe}^{3+}$  in the mill, the product does not irritate and it is compatible with the cement manufacture. The gypsum in the product can substitute part of the amount of gypsum normally used in cement manufacture.  
30

35 The following examples illustrate the invention, without restricting the same.

EXAMPLE 1

A test batch of appr. 1000 tons of raw ferrous sulphate hydrate from titanium dioxide pigment production which  
5 contained appr. 14 % by weight of  $\text{Fe}^{2+}$  and appr. 24 % by weight of sulphuric acid, was neutralized with cement (Partek Cement AB, Rapid) using an amount of 8 % by weight calculated from the ferrous sulphate hydrate. The  
10 mixing took place in a continuous concrete mixing plant. The mixing time was short, only a few seconds, whereafter the mixture was deposited for end reaction. Mixing took place without any disturbances from the materials used. An analysis of the end material showed that the  $\text{Fe}^{2+}$ -content was substantially the same and that essentially no  
15 oxidation to  $\text{Fe}^{3+}$  had taken place. The pH of the end product was 1.5.

EXAMPLE 2

20 Further test series have been carried out wherein raw ferrous sulphate has been neutralized with different materials and also using different combinations. In the series 1 - 10, the ferrous sulphate according to the Example 1 was treated first with 4 and 8 % by weight of  
25 limestone, respectively, and thereafter with 6 and 2 % by weight of Rapid cement, respectively, calculated from the ferrous sulphate. In the series 11 to 22, raw ferrous sulphate was mixed with various types of CaO-containing material in an amount of either 10 or 20 % by weight,  
30 calculated from the ferrous sulphate. The pH was measured (1 part by weight powder and 9 parts by weight water) after 1 day. The heat generation in the powder mixture was measured after a mixing time of 5 minutes. The results are given in the Tables 1 and 2.



TABLE 1

Types of limestone

A: Moist limestone  
 B: Parfil 1, Partek Cement AB  
 C: Parfil 6, -"-  
 D: Bypass-dust  
 E: Precipitator dust

|    |     |                    |   |      |          |      |
|----|-----|--------------------|---|------|----------|------|
| 5  | No. | Type of lime stone | % | pH   | Cement % | pH   |
| 10 | 1   | A                  | 4 | 1.51 | 6        | 1.80 |
|    | 2   | A                  | 8 | 1.58 | 2        | 1.70 |
|    | 3   | B                  | 4 | 1.58 | 6        | 1.81 |
| 15 | 4   | B                  | 8 | 1.64 | 2        | 1.72 |
|    | 5   | C                  | 4 | 1.62 | 6        | 1.77 |
|    | 6   | C                  | 8 | 1.67 | 2        | 1.73 |
| 20 | 7   | D                  | 4 | 1.67 | 6        | 1.93 |
|    | 8   | D                  | 8 | 1.73 | 2        | 1.86 |
|    | 9   | E                  | 4 | 1.65 | 6        | 1.90 |
| 25 | 10  | E                  | 8 | 1.75 | 2        | 1.84 |

The results show that limestone in the amounts used, was not reactive enough to sufficiently raise the pH, but that a sufficient pH raise is obtained with a further addition of cement. When mixing the limestone, a very small heat generation was obtained for the samples 1 to 6, for the samples 7 and 9 the maximum temperature was 32 °C and for the samples 8 and 10, it was 40 °C. When mixing the cement, the maximum temperature for the samples 1, 3, 5, 7 and 9 was appr. 60 to 80 °C, and for the remaining samples appr. 40 °C.

TABLE 2

| No.   | Additive                                    | %  | Temp.<br>°C | pH         |
|-------|---|----|-------------|------------|
| 5     |   |    |             |            |
| 11    | Rapid-cement                                | 20 | 780         | 3.3        |
| 12    | Salmisaari<br>desulphuration product        | 20 | 5           | 1.9        |
| 13    | Copper-slag sand                            | 20 | 30          | 1.8        |
| 10 14 | Special steel slag (602 m <sup>2</sup> /kg) | 0  | 50          | 1.7        |
| 15    | Ground steel slag (511 m <sup>2</sup> /kg)  | 20 | 60          | 2.3        |
| 16    | Steel slag (unground)                       | 20 | 35          | 1.7        |
| 17    | Blast furnace slag (404 m <sup>2</sup> /kg) | 10 | 69          |            |
| 18    | Mason's cement                              | 10 | 74          |            |
| 15 19 | Standard cement                             | 10 | 78          | 2.1(3d)    |
| 20    | Quick cement                                | 10 | 93          |            |
| 21    | Standard cement +<br>fly ash                | 10 | 5           | 79 2.3(3d) |
| 22    | Standard cement                             | 15 | 81          | 2.7(3d)    |

20 In the samples 19, 21 and 22, the ferrous sulphate had been pre-treated with 8 % by weight of limestone. From the results it can be seen i.a. that the temperature can be regulated by means of a suitable choice of cement type.

25 In the following Table 3, the pH and temperature increase (pH after one day and the maximum temperature of the mixture, respectively) in tests carried out by adding 10 %  
30 by weight of standard cement to three differently treated ferrous sulphate products, namely

- 35 1: ferrous sulphate treated with 8 % by weight of limestone  
2: ferrous sulphate treated with 8 % by weight of Rapid cement  
3: ferrous sulphate treated with 8 % by weight of limestone and thereafter with 8 % by weight of standard cement

40

| No. | Max. temp. | Start.prod.<br>pH | End prod.<br>pH |
|-----|------------|-------------------|-----------------|
| 1   | 90         | 1.58              | 1.98            |
| 2   | 33         | 1.86              | 2.80            |
| 3   | 22         | 2.95              | 4.04            |

The results show that for the products 2 and 3, a small or negligent temperature increase is obtained by means of the further addition of 10 % by weight cement, but that on the other hand the product 1 contains more free sulphuric acid.

### EXAMPLE 3

In this example, the capacity of the ferrous sulphate hydrate products made according to the process, namely products 2 and 3 from the Table 3 was measured. One part by weight of products 2 and 3, respectively, was mixed with 92 parts by weight of Rapid cement and 7 parts by weight of gypsum. The content of sixvalent chromium ( $\text{Cr}^{6+}$ ) was measured in the obtained product. Also the reduction capacity of the product was measured using the standard SFS 5183 (24.3.86) by adding to the mixture an excess of 50 mg/kg  $\text{Cr}^{6+}$  and measuring the amount of reduced chromium. Without the addition of extra chromium no measurable chromium content is obtained. The higher the value, the better reduction capacity of the product

| Sample | $\text{Cr}^{6+}$ | Reduction capacity |
|--------|------------------|--------------------|
| 2      | 0                | 39 mg/kg           |
| 3      | 0                | 37 mg/kg           |

By adding amounts between 0.5 to 1 % by weight of the product obtained according to the invention to various commercial cement types, reduction capacities up to 49 mg/kg could be measured using the above mentioned standard method. The ferrous content ( $\text{Fe}^{2+}$ ) in the treated

cement varied typically between 0.01 to 0.2 mg/kg. In the following table, a compilation of analysis results is presented from tests where ferrous sulphate hydrate has been added to cement with varying starting chromium content.

TABLE 4

|    | Cr <sup>6+</sup><br>mg/kg | Addition<br>% | Red. capacity<br>mg/kg | Fe <sup>2+</sup> in cement<br>% |
|----|---------------------------|---------------|------------------------|---------------------------------|
| 10 | 24                        | 0.7           | 6                      | 0.07                            |
|    | 14                        | 0.5           | 4                      | n.a.                            |
|    | 25                        | 0.5           | 13                     | n.a.                            |
| 15 | (Luja cement)             |               |                        |                                 |
|    | 25                        | 0.5           | 17                     | n.a.                            |
|    | (Rapid)                   |               |                        |                                 |

20 n.a. = not analyzed.

## Claims

1. Method for treating ferrous sulphate for the preparation of ferrous sulphate hydrate usable for chromium reduction in cement manufacture, characterized in that sulphuric acid containing ferrous sulphate obtained as a side product from titanium dioxide production and which contains at the most appr. 30 % by weight of sulphuric acid, is neutralized with a CaO containing material in an amount sufficient to give a pH value to the end product which is 1.5 to 5, whereby the reaction temperature is allowed to increase to at the most 120 °C.
2. The method according to the claim 1, characterized in that the CaO-containing material is used in an amount which gives an end pH value of 2.3 to 4.
3. The method according to the claim 1 or 2, characterized in that a temperature of at the most 105 °C is maintained.
4. The method according to any one of the claims 1 to 3, characterized in that the CaO-containing material is cement.
5. The method according to the claim 4, characterized in that limestone is used together with cement.
6. The method according to any one of the claims 1 to 5, characterized in that the starting ferrous sulphate is first treated with limestone or a smaller amount of cement, to a pH-value over appr. 1.4, and thereafter with cement to the end pH-value.
7. The method according to any one of the claims 1 to 5, characterized in that the starting ferrous sulphate is first treated with cement and optionally with limestone,

and thereafter with fly ash to improve the flow characteristics of the end product.

8. The method according to any one of the claims 1 to 7,  
5 **characterized** in that the starting ferrous sulphate is  
subjected to drying prior to the neutralization.

1  
INTERNATIONAL SEARCH REPORT

International application No.  
PCT/FI 96/00198

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC6: C01G 49/14

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

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**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages   | Relevant to claim No. |
|-----------|--|-----------------------|
| X         | GB 1581539 A (LAPORTE INDUSTRIES LIMITED),<br>17 December 1980 (17.12.80), claims 1-20<br><br>--                           | 1-8                   |
| A         | NO 8401942 A1 (AKTIESELSKABET AALBORG<br>PORTLAND-CEMENTFABRIK), 24 May 1984 (24.05.84),<br>claim 1, abstract<br><br>----- | 1-8                   |

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|   |                     | AU-A- 2926377              | 05/04/79            |
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| WO-A1- 8401942                            | 24/05/84            | AU-A- 2260183              | 04/06/84            |
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